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RESEARCH ARTICLE

# Analysis of Tar by Catalytic Pyrolysis of Waste Jute

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## ABSTRACT

Catalytic pyrolysis involves the production of upgraded liquids in a single step within short residence times. In the present study the catalytic pyrolysis of jute has been investigated using a cylindrical semi-batch pyrolyzer made of stainless steel under both isothermal condition and within the temperature range of 400$^0$C to 900$^0$C in an inert N2 atmosphere. Aluminium Oxide ($Al_2O_3$) was used as the catalyst. Alumina was pre-calcined at 120ºC for 2 hr in muffle furnace before being used in the reactor. Catalyst and jute were mixed directly in the ratio of 1:10. The use of $Al_2O_3$ catalyst led to higher tar yield and phenolic compounds in the liquid product. The chemical composition of the pyro – oil was analyzed by Fourier Transform Infrared spectroscopy to identify the basic compositional groups and Gas Chromatography/Mass Spectrometry to quantify the components. The energy yield of the pyro-oil has been calculated.

**Keywords:** Aluminum oxide, Productyiel, Pyrolysis kinetic, Pyrolysis, Energy yield, FTIR, GC/MS, Jute.

## 1. INTRODUCTION

In recent years biomass is considered to be a major source of renewable energy and takes part in climate change mitigation and energy security context. Biomass feed stocks like agricultural residues [1], municipal solid wastes[2],vegetable wastes[3], textile disposals [4] and energy crops have attracted great attention as renewable energy sources. Pungam oil cakes [5], jute waste [6],[7], soya bean [8], rape seed [9], sunflower oil cake [10], cotton [11] are used as renewable energy sources. Energy can be engendered from biomass through thermochemical conversion processes like combustion, pyrolysis, gasification etc. Pyrolysis is the thermochemical decomposition of organic materials at elevated temperatures in the absence of oxygen to produce solid char, liquid tar, and gases. Catalytic pyrolysis involves the production of upgraded liquids in a single step within short residence times. [12] investigated spruce wood pyrolysis in presence of seven mesoporous catalysts. The increased trend of gas yield and the aqueous part of tar yield has been observed in case of each catalytic experiment, but in case of char yield not so much changes has been observed in case of catalytic and non-catalytic experiment. [13] observed that the change in the composition of the volatiles is produced by the catalytic pyrolysis of biomass.[14] investigated the effect of hydrothermal pretreatment of biomass, the product yield and composition of bio-oil which is produced from the flash pyrolysis of the biomass. They have also reported the effect of catalytic up-gradation of pyrolysis vapours derived from the biomass. In the present work catalytic pyrolysis kinetics of jute in the temperature range of 400$^0$C to 900$^0$C in an inert N2 atmosphere decreases the activation energy. The use of $Al_2O_3$ catalyst led to higher tar yield and phenolic compounds are increased in the liquid products compared to non-catalytic pyrolysis. The simulated results of the model were compared with the experimental results satisfactorily.

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## 2. MATERIAL AND METHODS

### 2.1. Materials

The feedstock used for the investigations was jute. The density and energy appease in jute [6], [7] is higher than some woods available in the world. The volatile fraction and carbon gratify in jute is higher than many agricultural biomass. Both proximate analyses and ultimate analyses of the feed material were carried out and the analytical conclusions have been shown in table 1 along with the heating value and the bulk density of the feed material.

Table 1.The attributes of jute

| Proximate Analysis | Moisture | | Volatile Matter | Ash | Fixed Carbon | |
|---|---|---|---|---|---|---|
| % (W/W) | 3.1 | | 78 | 23 | 0.62 | |
| Ultimate Analysis | C | H | O | N | Cl | S |
| % (W/W) | 49.79 | 6.02 | 41.37 | 0.19 | 0.05 | 0.05 |
| Heating value (MJ /kg) | 19.7 | | | | | |
| Bulk Density (gm/ml) | 0.11 | | | | | |

### 2.2. Catalytic materials

The catalytic material used for these experiments is Aluminium Oxide ($Al_2O_3$) [14]. It was previously calcined at 120ºC for 2 hrs in a muffle furnace. It has a relatively high thermal conductivity (30 Wm−1K−1).

### 2.3. Equipment and Experimental Set-Up

The pyrolysis of jute sample has been done by following the procedure described in [6].

## 3. Theoretical Analysis

### 3.1Pyrolysis Kinetics

Pyrolysis of lignocellulosic materials ensues by the complex reactions in series, parallel or combination of both. [15], [16]. The reaction pathway of pyrolysis has been given below:

$$Jute + Catalyst \rightarrow Active\ Complex \begin{matrix} \xrightarrow{k_v} Volatile \\ \xrightarrow[k_c]{} Char \end{matrix} \quad (3.1)$$

Therefore,

$$\frac{dW}{dt} = -kW \quad (3.2)$$

$$\frac{dW_V}{dt} = -k_v W \quad (3.3)$$

$$\frac{dW_c}{dt} = -k_c W \quad (3.4)$$

where $k = k_v + k_c$

The rate constants k, kv and kc have been determined through non-linear regression analysis of experimental data of captive sampling experiments following the methods described by [11]. The frequency factors and activation energies are given in table 2.The analysis is shown in equations (3.1),(3.2),(3.3),(3.4) and (3.5).

Table 2.The Activation energies and frequency factors of the experiment

| | A | E |
|---|---|---|
| K | 0.863898 | 34.77414 |
| $K_v$ | 1.231952 | 40.44761 |
| $K_c$ | 0.027223 | 16.8558 |

### 3.2. Energy Yield

The energy yield of pyro–oil obtained at different pyrolysis temperatures have been determined using the following correlation,

$$Energy\ Yield(\%) = \frac{w_l \times C_{V_{oil}}}{C_{V_{biomass}}} \times 100 \quad (3.5)$$

where, $w_l$ = yield (weight fraction) of pyro – oil

CVoil= Calorific Value of pyro – oil (MJ/Kg)

CVbiomass= Calorific Value of jute (MJ/Kg)

## 4. RESULTS AND DISCUSSION

### 4.1. Trend of pyrolysis product yield and product characteristics

From the analysis of experimental data, it was observed in Figure B1 that yield of char is increased at 973 K. From 1073 K to 1173K it remained constant. The yield of tar is maximum at 1173K. On the other hand yield of gas is maximum at 873 K. From 1073 K to 1173 K it remained constant.

The use of $Al_2O_3$ catalyst led to higher tar forgo and phenolic compounds are increased in liquid products compared to non-catalytic pyrolysis. Catalytic pyrolysis involves the production of upgraded liquids in a single step within short residence times. The simulated results of the model were compared with the experimental eventuates satisfactorily.

### 4.2. Energy Yield

The values of energy yield of pyro – oil have been plotted against temperature in figure 1. From the analysis of the figure it shows that the increase in co-pyrolysis temperature results in the increase of energy yield with respect to pyro-oil. It is due to the fact that with the increase of co-pyrolysis temperature the tar becomes richer in carbon which leads to the increase in specific energy content.

### 4.3. Fourier Transform Infrared Spectroscopy (FTIR) Analysis of jute Tar

The functional groups of the pyro – oil obtained at temperature of 700OC or 973K was estimated by Fourier Transform Infrared (FTIR) spectroscopy to classify the basic compositional classes shown in figure B2.

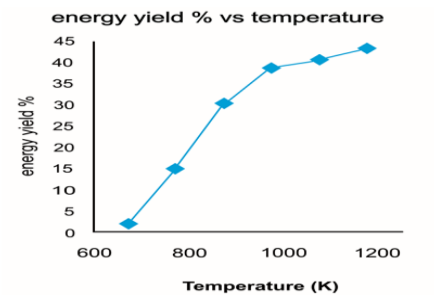


Figure 1.Energy yield variation with temperature change

Based on the FTIR results, the functional groups and the indicated composition of the liquid products are bestowed in table 3.

From the close analysis of the table, it appears that the bio-oil is highly oxygenated as indicated by the predominance of oxygenated functional groups namely O – H; C=O; C – O and aromatic compounds. This is also established by the elemental composition (not shown) and the acidic nature, indicated by low value of pH. The high fraction of oxygenated compounds causes the lowering of calorific value of the oil, particularly due to the presence of C=O bonds which do not release energy during combustion [18]. The presence of hydrocarbon groups C – H; C = C; and alcohols reveals that the liquid have a potential to be used as sustenance. The results of FTIR analysis is comparable to those obtained by [6], [17] during their studies on pyrolysis of wastes.

### 4.4. Pyrolysis GC/MS

The qualitative classification and quantitative computation of the pyro-oil, which embodies the volatile and semi volatile components was analyzed by SQ 8 Gas Chromatograph/Mass Spectrometer[19], equipped with flame ionization and mass spectrometry detection (GC-PPC-MS). The following figure B3 along with table A1 depicts the formation of the compounds along with the retention times.

Table 3.FTIR functional groups and the indicated compounds of jute Tar.

| Frequency Range ($cm^{-1}$) | Groups | Class of compounds |
|---|---|---|
| 3600 – 3200 | O – H stretching | Polymeric O – H |
| 3050 – 2800 | C – H stretching | Alkanes |
| 1775 – 1650 | C = O stretching | Ketones, Aldehydes, Carboxylic acids |
| 1680 – 1575 | C ≡ C stretching | Alkenes |
| 1550 – 1475 | $-NO_2$ stretching | Nitrogenous compounds |
| 1490 – 1325 | C – H stretching | Alkanes |
| 1300 – 950 | C – O stretching, O – H bending | Primary, Secondary and Tertiary alcohols Phenols, esters, ethers |
| 900 – 650 | - | Aromatic compunds |
| 900 – 650 | - | Aromatic compunds |

## 5. CONCLUSION

In the present investigation, catalytic pyrolysis of jute has been studied in the temperature range of 400$^0$C to 900$^0$C in the presence of Aluminum Oxide ($Al_2O_3$). Tar yield is much higher when used with catalyst compared to using without catalyst. The fraction of oxygen decreases in the bio-oil which is also termed as pyro-oil, with the application of suitable catalysts. The chemical configuration of pyro – oil was cross checked by FTIR and GC/MS. Catalytic pyrolysis improved the production of upgraded liquids in a single step within short residence times.

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# APPENDIX A

Table A1.GC/MS analysis of the bio-oil

| Retention Time (min) | Name of compound | Molecular Weight (g/mol) |
|---|---|---|
| 3.258 | Hydrazine, Trimethyl- | 74 |
| 3.313 | Silane, Butyl Trimethyl - | 130 |
| 3.353 | Silane, Trimethyl propyl - | 116 |
| 4.999 | 1H –Imidazole – 4 - methanol | 98 |
| 5.054 | Cyclopenteane, 1 – Hydroxymethyl - 1,3 – dimethyl - | 128 |
| 5.114 | Levoglucosenone | 126 |
| 6.025 | Trans, Trans and trans, Cis - 1,8 – Dimethyl spiro [5,5] undecane | 180 |
| 6.345 | 2,2 – Dimethyl hex – 4 - Enylamine | 127 |
| 7.245 | Trans, Cis -1,8 – Dimethyl spiro [4,5] Decane | 166 |
| 7.620 | 2 – cyclopenten -1- one, 2,3 - dimethyl | 110 |
| 8.145 | Pyrimidine, 5 – methyl | 94 |
| 9.016 | D - limonene | 136 |
| 9.701 | p-cresol | 108 |
| 10.026 | Silane, Tetraethenyl | 136 |
| 11.952 | 1,3,2 – Dioxaborolane, 2 – phenyl- | 148 |
| 12.252 | (Z) – 4- Methyl – 5 – (2-oxo propylidene) – 5H – Furan – 2 – one | 152 |
| 13.713 | Formic acid, 2,6 – dimethoxy phenyl ester | 182 |
| 14.233 | Phenol, 2, 6 – Dimethoxy - | 154 |
| 15.488 | 4-methoxy – 2-methyl – 1-(methylthio) benzene | 168 |
| 16.709 | 1- acetyl – 3 – (4 – pyridyl) - pyrazoline | 189 |
| 17.244 | N-nitrosonornicotine | 177 |
| 17.824 | 2 - propen -1 – one, 2 – methyl – 1 – phenyl | 146 |
| 19.170 | 2 – ethyl – 2 - phenylaziridine | 147 |
| 20.946 | 2 – methyl benzyl phosphonic acid | 186 |
| 21.131 | 5 - phenylisoxazoline | 147 |
| 21.701 | Trans – 1 – cyano – 2 – phenyl cyclopropanol | 159 |
| 22.231 | 2,5,6 - trimethylbenzimidazole | 160 |

## APPENDIX B

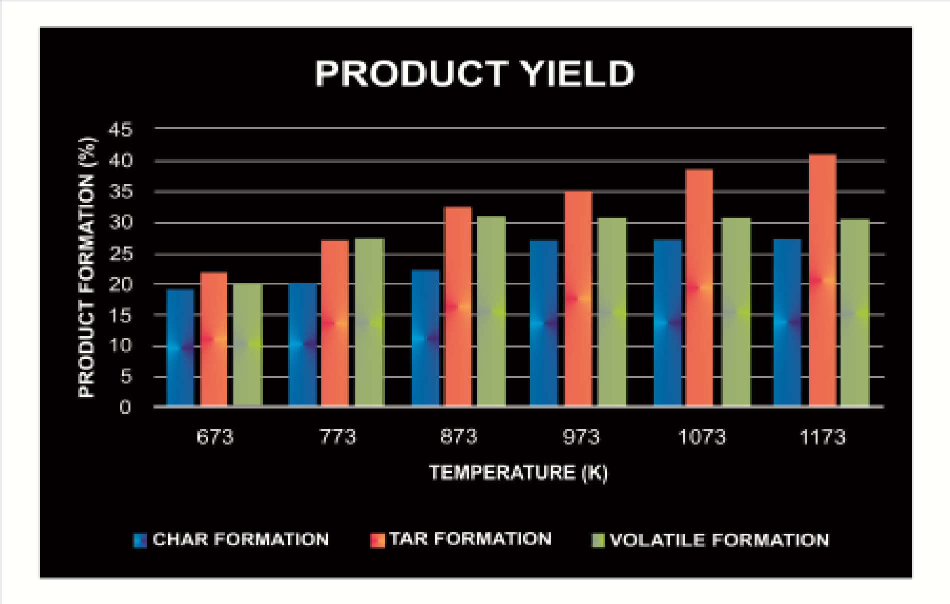


Figure B1.Catalytic Pyrolysis and product characterisation

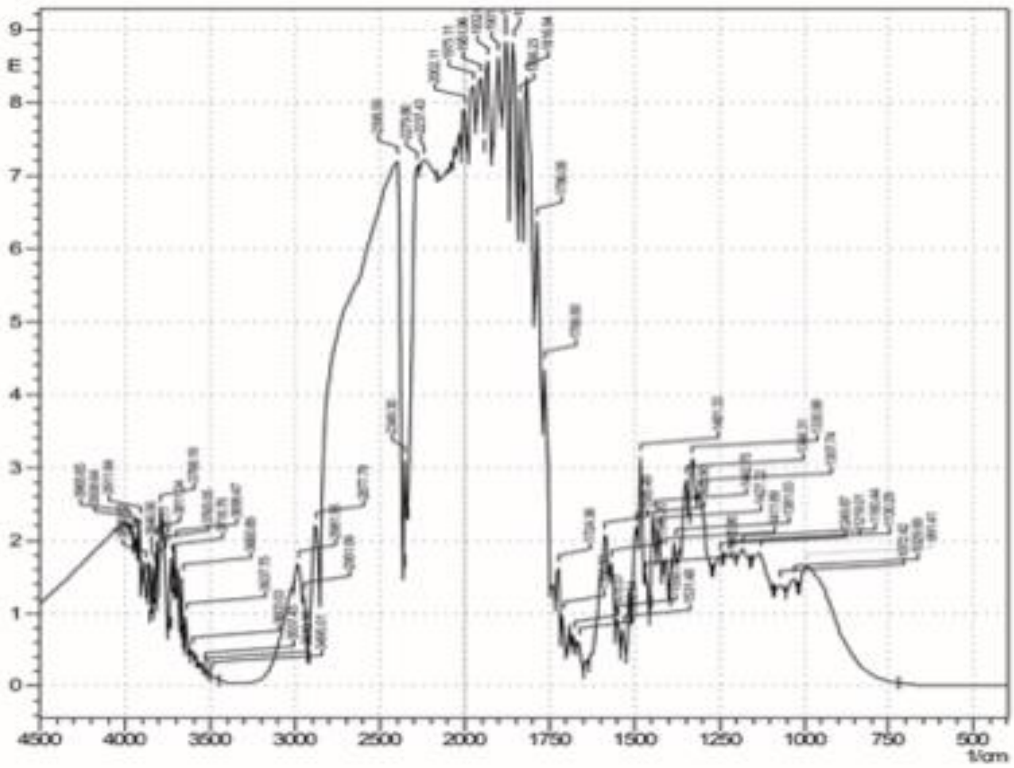


Figure B2.FTIR investigation of pyrolysis of jute at 7000C or 973K.

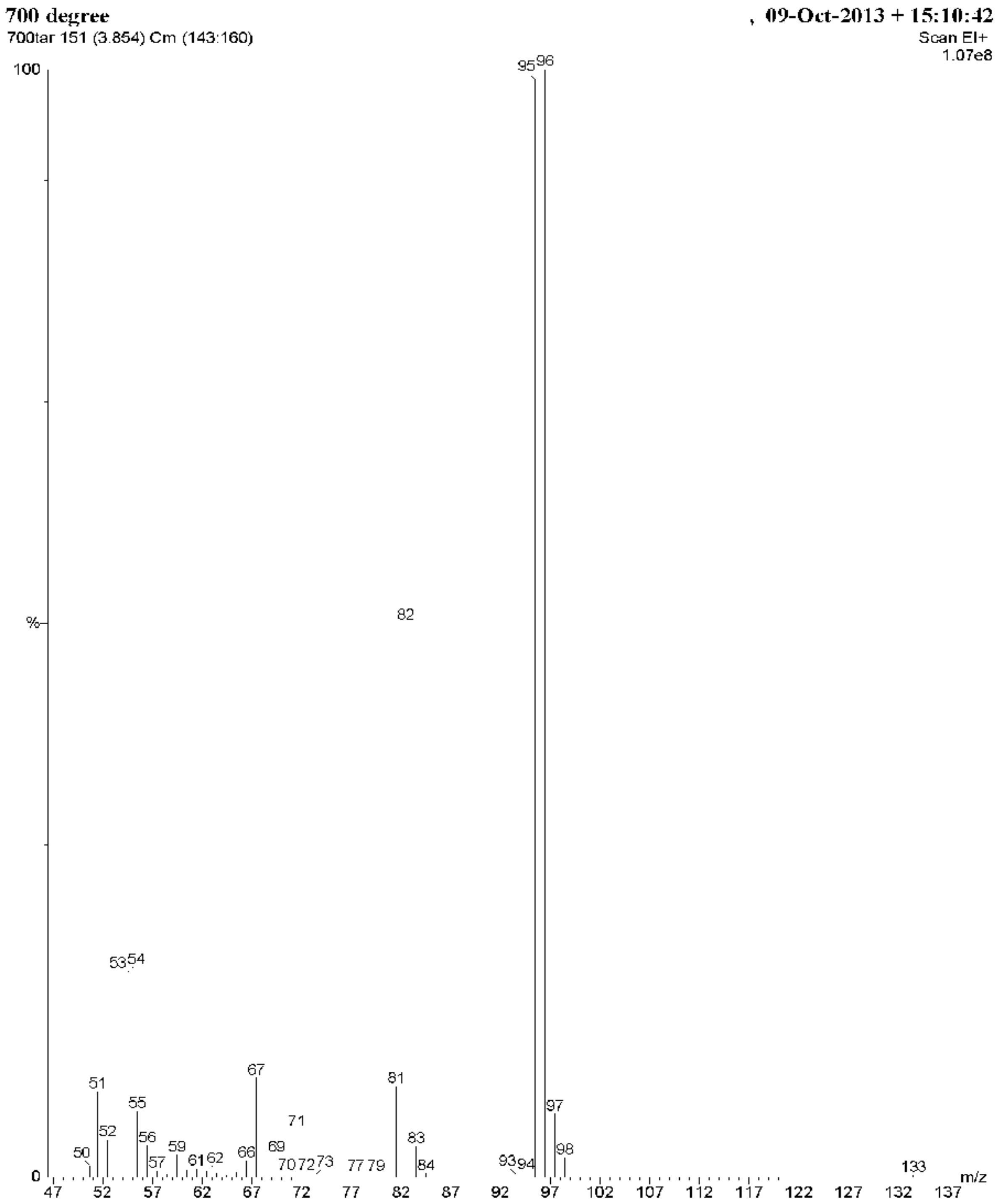


Figure B3.Chromatogram of the Product